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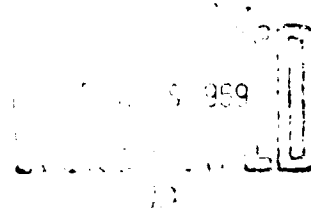
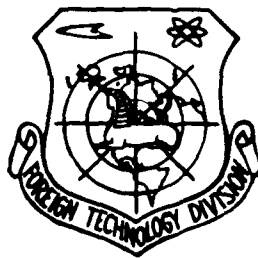
## FOREIGN TECHNOLOGY DIVISION



APPLICATION OF CERTAIN SHALE PRODUCTS AS CORROSION INHIBITORS

by

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## EDITED TRANSLATION

APPLICATION OF CERTAIN SHALE PRODUCTS AS CORROSION  
INHIBITORS

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ABSTRACT <p>→ The effect of H<sub>2</sub>O-sol. shale phenols on the corrosion of C steel in aq. solns. of AcOH, NH<sub>4</sub>Cl, K<sub>2</sub>SO<sub>4</sub>, HCl, KCl, and H<sub>2</sub>SO<sub>4</sub> was studied. The corrosion rate decreased by a factor of 5-25. A shale de-emulsifier used in the desalination of oils had an analogous action. The presence of a shale de-emulsifier in an amt. of 5 g./l. in a 0.5N H<sub>2</sub>SO<sub>4</sub> soln. decreased the corrosion of C steel from 23 to 1.5 g./m.<sup>2</sup> hr. From Ref. Zh., Khim. 1967, Pt. II, Abstr. No. 5P80.</p>				

## APPLICATION OF CERTAIN SHALE PRODUCTS AS CORROSION INHIBITORS

R.E. Metsik, *Candidate of Technical Sciences*

At present, the shale industry is producing water-soluble phenols that are obtained by extraction with butyl acetate from tar water and used as a raw material for the production of synthetic tanning agents and adhesives of type DFK. These water-soluble phenols consist chiefly of dimethylresorcinols. The content of monophenols (phenol, cresol and other water-soluble monophenols) in the mixture is only 10-15%, and the remaining components are bifunctional water-soluble phenols.

TABLE 1

### Decrease in Rate of Corrosion of Carbon Steel in Hydrochloric Acid on Addition of 6 g/liter of Phenols

1	2	3
Характеристика среды	Скорость при 20°C. мм/год	Эффект ингиби- тора, %
4 0,1 н. раствор соляной кислоты .	0,13	95
1,0 н. » » » » .	0,04	96
0,01 н. » » » » .		
5 насыщенной сероводородом .	0,22	98

- 1) Description of medium
- 2) Rate at 20°C, mm/year
- 3) Effect of inhibitor, %

- 4) 0.1N hydrochloric acid
- 5) Saturated with hydrogen sulfide

It was noted in the corrosion laboratory of the Shale Institute that the corrosion of steel is reduced to a fraction in the presence of small quantities of the above phenols in acidic aqueous solutions and in butyl acetate. This indicates a possibility of using phenols as corrosion inhibitors.

Gravimetric studies showed that the corrosion rate of carbon steel in acidic aqueous solutions is reduced by factors of 5-25 under the influence of shale phenols, with the inhibitor effect reaching 98% in certain cases (Tables 1 and 2).

TABLE 2

Decrease in Corrosion Rate of Carbon Steel in Acidic Salt Solutions Under the Influence of Phenols at 20°C

A Состав раствора, мг-экв/л					pH	B Количество добавленных фенолов, г/л	C Скорость коррозии в растворе, мм/год	
CH <sub>3</sub> COOH	NH <sub>4</sub> Cl	K <sub>2</sub> SO <sub>4</sub>	HCl	KCl			не содержа- щем фенолы	содержа- щем фенолы
11	25	35	100	—	1,0	7,0	2,54	0,12
—	60	—	100	30	1,3	4,3	2,68	0,12
11	25	20	—	—	3,4	1,0	0,50	0,10
5	25	20	—	—	4,7	2,0	0,58	0,07
11	25	—	—	25	3,4	0,1	0,50	0,30

A) Solution composition,  
mg-eq/liter

B) Amount of phenols added,  
g/liter

C) Corrosion rate in solution,  
mm/year

D) Not containing phenols

E) Containing phenols

TABLE 3

Rectification Data of Phenols and  
Characterization of Fractions  
Obtained

1 Пределы кипения, °C		4 Выход фракций, %	5 Содерж- жание группы ОН, %	6 Молеку- лярный вес
2 при 15 мм рт. ст.	3 и пересчете на атмос- ферное дав- ление			
75—145	170—260	15,6	13,1	118
145—161	260—280	9,2	19,5	130
161—165	280—285	7,1	23,8	134
165—169	285—290	26,5	24,6	138
169—173	290—295	16,8	24,4	141

1) Boiling range, °C

2) At 15 mm Hg

3) Converted to atmospheric  
pressure

4) Yield of fraction, %

5) OH-group content, %

6) Molecular weight

It is seen from polarization curves that corrosion is reduced in hydrochloric acid under the influence of the phenols chiefly as a result of cathode-process inhibition.

The phenols were rectified (Table 3) to determine the inhibitor properties of the individual fractions. Bifunctional phenols were obtained by separating the total phenols on silica gel by distributive solvent (benzene and methanol) chromatography.

Gravimetric studies indicated (Table 4) that all phenol fractions have almost identical inhibiting properties, with the inhibitor effect above 90% in all cases. Increasing the amount of

TABLE 4

Protective Effect of Phenols in  
Corrosion of Carbon Steel in 0.1n  
Hydrochloric Acid

A Наименование присадки	B Количество присадки, г/л			
	1	5	1	5
	C Скорость коррозии, мм/год		D Эффект ингибитора, %	
E Суммарные фенолы . . . .	0,14	0,17	94	93
F Двухатомные фенолы . . . .	0,18	0,09	93	96
G Фракция фенолов 170— 260° C	0,20	0,08	91	97
Фракция фенолов 260— 280° C	0,15	0,05	94	98
Фракция фенолов 280— 285° C	0,16	0,06	93	97
Фракция фенолов 285— 290° C	0,37	0,07	85	97
Фракция фенолов 290— 295° C	0,13	0,06	95	97

A) Additive

E) Amount of additive, g/liter

C) Corrosion rate, mm/year

D) Inhibitor effect

E) All phenols

F) Bifunctional phenols

G) ...°C phenol fraction

TABLE 5

Inhibitor Effect in Pickling of  
Steel in the Presence of Phenols,  
%

A Количе- ство фенолов, г/л	B Серная кисло- та, 10%		B Серная кисло- та, 20%		D Соляная кислота, 10%	
	C при 20° C	C при 60° C	C при 20° C	C при 60° C	C при 20° C	C при 60° C
10	72	79	60	65	60	67
30	95	81	96	93	86	80
40	98	97	98	97	91	85

A) Amount of phenols, g/liter

B) Sulfuric acid

C) At

D) Hydrochloric acid

additive from 1 to 5 g/liter lowers the corrosion of carbon steel  
in all cases in 0.1n hydrochloric acid.

It is seen from Table 5 that water-soluble shale phenols can  
be used as corrosion inhibitors for pickling of carbon steel in  
sulfuric acid.

Shale deemulsifiers may become one of the methods of protect-

ing metals from corrosion.

A shale deemulsifier is a 45% solution of the sodium or ammonium salts of shale-tar sulfo acids. At the present time, this material is being produced by the shale refinery at Syzrany and is used in the petroleum industry as a deemulsifier for desalting of petroleum.

Study of this material in the corrosion laboratory of the ESSR Shale Institute showed that the deemulsifier has inhibitor properties.

The presence of 5 g/liter of shale deemulsifier in 0.5n sulfuric acid solution lowers the corrosion of carbon steel from 23 to 1.5 g/m<sup>2</sup>·h. In solutions of chlorides and sulfates (pH 2), the corrosion rate of carbon steel is lowered from 0.38 to 0.03 g/m<sup>2</sup>·h with an inhibitor effect higher than 90% under the influence of 1 g/liter of shale deemulsifier.